Metal Speciation of Smelter-Contaminated Soils of Deer Lodge County, Montana

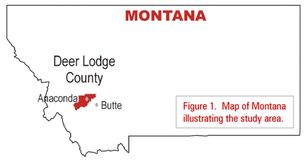
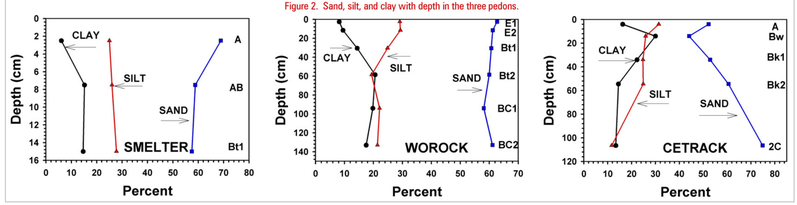


Figure 1. Map of Montana illustrating the study area.

Figure 2. Sand, silt, and clay with depth in the three pedons.



INTRODUCTION

The Butte district in Montana (Fig. 1) was one of the major mining districts of the world with continuous production from underground and open pit mines from 1864 to 1983 (Glasscock, 1935; Malone, 1981). More than a century of mining and smelting precious ores, primarily copper, has resulted in metal contamination by many point sources and by different modes of distribution (air and water) in the Upper Clark Fork Basin (Harkins and Swain, 1907; Taskey, 1972).

In an earlier study (Burt, et al., 2000) in Deer Lodge County, total analysis indicated elevated levels of trace elements, with the general trend Cu > As > Zn > Pb. These elements were concentrated in the upper few centimeters, with a dramatic decline below this depth. Elements generally decreased with distance from the smelter, though concentrations were also related to protection from smelter smoke by topographic features and wind and smoke dispersal patterns.

Scientists with the Deer Lodge County Soil Survey were responsible for mapping and developing interpretations for land use and management in the area where smelting and related activities have affected every major soil interpretation. Trace element concentrations could not be correlated with apparent impacts on vegetation (e.g., species, growth, and vigor) or soil chemical properties (e.g., pH, base saturation). Upland soils were therefore mapped on the basis of impact classes (severe, moderate, and slight).

A better understanding of the fate, bioavailability, and transport of trace elements in these soils is required. Such information is commonly assessed using selective sequential extraction methods (Tessler, et al., 1979; Miller, et al., 1986; Rauret, et al., 1988). These methods do not provide a direct characterization of metal speciation, but rather indicate chemical reactivity (Ramos, et al., 1994). Sequential extractions generally use a series of reagents of increasing reactivity in the dissolution process. Metals extracted are then associated with a specific chemical pool, the assignment of which is based on the extraction of pure chemical substances during method development (Ramos, et al., 1994).

This study attempts to define the chemical forms of metals in selected pedons of Deer Lodge Valley. The objectives are to: (a) use sequential selective dissolution on three soils to provide information concerning the chemical forms and potential reactivity of these elements, and (b) test the utility of x-ray diffraction analysis of the sand fraction to supplement the chemical dissolution data relative to the crystalline mineral forms present. Understanding trace elemental forms in these soils may enable field scientists to improve land-use interpretations for mapping units in these contaminated areas.

MATERIALS & METHODS

Pedons were described by standard soil survey methods (Soil Survey Division Staff, 1993) and sampled and analyzed using procedures described in the Soil Survey Investigations Report (SSIR) No. 42 (Soil Survey Staff, 1996). Pedons were classified by U.S. Soil Taxonomy (Soil Survey Staff, 1999). All standard analyses were performed on air-dried <2-mm soil with resulting data reported on an oven-dry basis.

Sequential chemical fractionation (Table 1) is based on procedures of Tessier, et al. (1979) and Keller and Vedy (1994). The procedure was used to determine different fractions of Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn. Total concentration of these trace elements was also determined on a separate sample (< 80-mesh) by acid digestion (HNO_3 + HCl) in a microwave. Elements were analyzed by ICP-AES.

High density minerals in the very fine (0.05-0.1 mm), fine (0.10-0.25 mm), and medium sand (0.25-0.50 mm) particle size separates were separated from a lighter fraction with sodium polytungstate (density > 2.89g cm^{-3}) in a 30-ml separatory funnel. Heavy minerals were combined from the three fractions, mounted on a glass slide, and x-rayed from 2 to 80° 2-theta using Cu-Kα radiation.

Other characterization analyses performed were: particle-size analysis, organic C by acid-dichromate digestion and $FeSO_4$ titration, pH in H_2O, cation exchange capacity (CEC) with NH_4OAc buffered at pH 7.0 (CEC-7), with individual cations (Ca, Mg, K, and Na) determined by ICP-AES. Base saturation (pH 7) was determined by dividing the sum of NH_4OAc extractable bases by CEC-7 and multiplying by 100. Dithionite-citrate extracts were analyzed for Fe, Al, and Mn by atomic absorption spectroscopy.

RESULTS & DISCUSSION

Soils are generally sandy, with textures ranging from coarse sandy loam to clay loam (Fig. 2 a, b, c). The Smelter and Worock pedons range in pH from 4.0 to 5.7 (Fig. 3), while the Cetrack soil is alkaline, with carbonates ≥ 250 g kg^{-1} from 8 to 61 cm (Table 2). The pH of all soils is more acidic in the surface horizon. Base saturation of the surface horizon of Smelter and Worock pedons is 14 and 11 percent, respectively.

Total metals in the <2-mm fraction (Table 3) in all three pedons follow the general trend Cu > Mn > Zn > Pb > Cd > Cr > Co. This same trend appears for the water soluble fraction (data not shown) and suggests a relationship between total metals and concentration of a soluble, mobile metal fraction.

The Smelter pedon has the highest concentration of trace elements (Table 3) and these elements are elevated in all three horizons sampled relative to the other pedons. Cd, Cu, Pb, and Zn concentrations in the Worock and Cetrack pedons are elevated in the upper 20 cm and concentrations decrease and remain generally constant with depth. Other metals (Co, Cr, and Ni) typically have uniform surface and subsurface concentrations suggesting limited deposition from the smelter.

Table 1. Designated partition and chemical reagents used for sequential extraction of metals in selected horizons.

Partition	Reagents
Hydrosoluble	H_2O
Exchangeable	0.1 M $NaNO_3$
Carbonate-bound	1 M NaOAc, adjusted to pH 5 with HOAc
Fe-Mn oxide-bound	1 M NH_2OH·HCl in 25% v/v HOAc
Organic-bound	0.02 M HNO_3; 30% H_2O_2, adjusted to pH 2; wash with 3.2 M NH_4OAc in 20% v/v HNO_3
Residual	Concentrated HNO_3 + HCl (microwave digestion)

Table 2. Selected properties of three pedons in Deer Lodge Valley, Montana.

Horizon	Depth	Org. C	CEC (pH 7)	Base Sat. (pH 7)	Dithionite-Citrate			$CaCO_3$
	cm	g/kg	cmol/kg	%	Fe	Al	Mn	
					g/kg			
Smelter (S96MT-023-004)[1]; Loamy-skeletal, mixed, active Ustic Haplocryalf[2]								
A	0-5	7.2	8.6	14	15	2	2	n.d.[3]
AB	5-10	8.4	12.9	64	14	3	2	n.d.
Bt1	10-20	7.1	13.1	66	13	2	2	n.d.
Worock (S91MT-023-001); Loamy-skeletal, isotic Ustic Haplocryalf								
E1	0-5	80.9	25.7	11	4	1	Tr	n.d.
E2	5-18	4.7	10.8	49	3	1	Tr	n.d.
Bt1	18-43	3.0	16.1	80	3	Tr	--	n.d.
Bt2	43-74	2.9	24.0	93	2	Tr	--	n.d.
BC1	74-114	1.1	34.8	97	2	Tr	--	n.d.
BC2	114-152	0.8	30.0	96	2	Tr	--	n.d.
Cetrack (S91MT-023-005); Loamy-skeletal, mixed, active Typic Calcicryoll								
A	0-8	16.8	16.7	100	7	1	Tr	n.d.
BW	8-20	18.4	11.5	100	2	Tr	--	470
BK1	20-48	8.6	6.6	100	1	Tr	--	490
BK2	48-61	4.7	9.1	100	2	--	--	250
2C	61-152	0.6	8.6	100	6	Tr	Tr	80

[1] USDA-NRCS Soil Survey Number (Soil Survey Staff, 1995).
[2] Soil Survey Staff, 1999.
[3] n.d. = not determined; Tr = trace; "--" = determined, below detection limits.

Table 3. Analysis of total metals in < 2-mm fraction (Aqua regia digestion).

Horizon	Cd_T	Co_T	Cr_T	Cu_T	Ni_T	Pb_T	Zn_T	Mn_T
	mg/kg							
Smelter								
A	9.2	3.1	14.2	1270.1	8.1	474.5	849.2	397.7
AB	6.4	6.1	17.0	1008.2	9.1	149.6	442.6	578.6
Bt1	9.9	5.0	17.1	374.3	11.1	22.9	553.7	491.6
Worock								
E1	3.0	3.3	14.2	703.4	10.1	433.3	166.6	227.3
E2	0.9	4.4	16.8	25.9	14.1	10.4	98.5	197.7
Bt1	--[+]	4.5	20.7	9.8	14.3	8.5	36.0	105.6
Bt2	--	3.8	21.6	9.1	14.0	8.6	34.4	106.1
BC1	--	4.1	21.3	9.2	15.9	9.3	39.5	138.4
BC2	--	4.4	21.0	10.2	15.5	9.5	37.0	145.8
Cetrack								
A	3.4	5.3	16.1	591.6	12.3	71.6	328.6	506.7
Bw	--	3.3	10.3	36.2	14.0	4.5	35.0	96.9
Bk1	--	2.8	7.8	19.8	11.5	2.7	20.9	57.1
Bk2	--	3.5	10.8	15.3	14.3	4.1	25.7	122.1
2C	--	3.1	10.4	10.3	10.8	5.8	30.9	149.4

[+] "--" = conc. below detection limits.

Table 4a. Sequential extractions of Cu.

HZ	Cu_{wrs}	Cu_{ex}	Cu_{car}	Cu_{ox}	Cu_{om}	Cu_{res}	Cu_{sum}[1]	Recovery[2] (%)
	mg/kg							
Smelter								
A	0.5	75.5	n.d.[3]	1051.2	330.3	156.3	1613.8	127
AB	20.5	111.8	n.d.	955.9	98.7	73.2	1260.0	125
Bt1	5.6	11.5	n.d.	321.9	36.7	37.3	413.0	110
Worock								
E1	7.3	16.0	n.d.	361.4	238.9	92.7	716.4	102
E2	0.4	0.0	n.d.	8.0	4.4	11.3	24.0	93
Bt1	0.4	0.0	n.d.	0.8	1.0	7.0	9.2	94
Bt2	0.3	0.0	n.d.	0.8	1.3	7.0	9.4	104
BC1	0.2	0.0	n.d.	0.9	1.8	7.0	9.9	107
BC2	0.4	0.0	n.d.	0.4	7.2	7.0	15.0	147
Cetrack								
A	8.3	7.3	184.0	183.4	99.1	127.7	609.9	103
BW	0.6	0.0	0.9	1.3	1.8	13.2	17.7	49
BK1	0.5	0.0	1.1	2.4	1.3	11.2	16.5	83
BK2	0.8	0.0	0.2	0.9	1.3	8.1	11.2	73
2C	0.7	0.0	0.0	0.5	0.9	7.2	9.4	91

[1] Cu_{sum} = Sum of Cu from fractions (ws, ex, car, ox, om, res). [2] Recovery = Cu_{sum}/Cu_T. [3] n.d. = not determined.

Table 4b. Sequential extractions of Zn.

HZ	Zn_{wrs}	Zn_{ex}	Zn_{car}	Zn_{ox}	Zn_{om}	Zn_{res}	Zn_{sum}[1]	Recovery[2] (%)
	mg/kg							
Smelter								
A	0.0	77.1	n.d.[3]	189	592.9	388.2	1247.3	147
AB	18.4	119.2	n.d.	216	100.8	114.0	568.4	128
Bt1	16.7	121.1	n.d.	420	84.4	88.7	730.5	132
Worock								
E1	1.0	13.7	n.d.	32.7	63.4	76.7	187.5	113
E2	0.0	3.8	n.d.	17.0	20.5	59.3	100.6	102
Bt1	0.0	0.0	n.d.	0.8	2.9	37.7	41.5	115
Bt2	0.0	0.0	n.d.	0.3	4.0	35.5	39.8	116
BC1	0.0	0.0	n.d.	0.5	3.7	39.3	43.5	110
BC2	0.0	0.0	n.d.	0.1	3.3	42.2	45.6	123
Cetrack								
A	0.9	0.9	67.7	96.6	84.0	99.0	349.2	106
BW	0.0	0.0	0.4	0.9	1.7	26.1	29.2	83
BK1	0.6	0.0	0.3	0.9	1.3	22.4	25.5	122
BK2	0.0	0.0	0.3	0.9	1.9	24.4	27.6	107
2C	0.0	0.0	0.1	0.5	1.9	37.3	39.8	129

[1] Zn_{sum} = Sum of Zn from fractions (ws, ex, car, ox, om, res).
[2] Recovery = Zn_{sum}/Zn_T.
[3] n.d. = not determined.

Table 4c. Sequential extractions of Pb.

HZ	Pb_{wrs}	Pb_{ex}	Pb_{car}	Pb_{ox}	Pb_{om}	Pb_{res}	Pb_{sum}[1]	Recovery[2] (%)
	mg/kg							
Smelter								
A	0.0	6.3	n.d.[3]	412.9	2.4	120.4	541.9	114
AB	1.6	1.8	n.d.	163.8	7.6	17.4	192.1	128
Bt1	0.3	0.2	n.d.	23.1	1.6	5.3	30.5	133
Worock								
E1	2.2	4.8	n.d.	430.1	36.1	22.2	495.4	114
E2	0.0	0.0	n.d.	6.0	0.8	4.7	11.5	111
Bt1	0.0	0.0	n.d.	2.4	0.7	5.4	8.5	100
Bt2	0.0	0.0	n.d.	2.3	0.4	6.2	9.0	104
BC1	0.0	0.0	n.d.	2.1	1.0	6.9	10.0	107
BC2	0.0	0.0	n.d.	2.4	1.0	9.7	13.2	140
Cetrack								
A	0.4	0.5	17.2	46.1	5.2	9.7	79.2	110
BW	0.0	0.0	0.0	2.6	0.3	1.7	4.7	103
BK1	0.0	0.0	0.4	2.9	0.2	3.3	6.9	259
BK2	0.1	0.0	0.6	2.6	0.3	2.3	6.0	146
2C	0.0	0.0	0.5	2.8	0.5	2.7	6.6	114

[1] Pb_{sum} = Sum of Pb from fractions (ws, ex, car, ox, om, res).
[2] Recovery = Pb_{sum}/Pb_T.
[3] n.d. = not determined.

Table 4d. Sequential extractions of Cr.

HZ	Cr_{wrs}	Cr_{ex}	Cr_{car}	Cr_{ox}	Cr_{om}	Cr_{res}	Cr_{sum}[1]	Recovery[2] (%)
	mg/kg							
Smelter								
A	0.00	0.04	n.d.[3]	1.32	1.20	15.07	17.6	127
AB	0.12	0.07	n.d.	0.95	2.34	17.46	20.9	125
Bt1	0.13	0.06	n.d.	0.61	2.44	17.71	20.9	110
Worock								
E1	0.02	0.00	n.d.	0.42	2.68	12.10	15.2	102
E2	0.02	0.00	n.d.	0.42	1.04	15.17	16.7	93
Bt1	0.06	0.03	n.d.	0.22	1.37	19.84	21.5	94
Bt2	0.07	0.04	n.d.	0.23	2.12	19.11	21.6	104
BC1	0.06	0.03	n.d.	0.27	2.64	19.16	22.1	107
BC2	0.05	0.03	n.d.	0.25	2.37	20.81	23.5	147
Cetrack								
A	0.03	0.04	0.05	0.45	2.20	15.35	18.1	103
BW	0.00	0.02	0.05	0.13	1.64	8.70	10.5	49
BK1	0.01	0.02	0.07	0.14	1.09	7.07	8.4	83
BK2	0.02	0.01	0.03	0.23	0.96	9.75	11.0	73
2C	0.00	0.04	0.00	0.14	0.97	9.79	10.9	91

[1] Cr_{sum} = Sum of Cr from fractions (ws, ex, car, ox, om, res).
[2] Recovery = Cr_{sum}/Cr_T.
[3] n.d. = not determined.

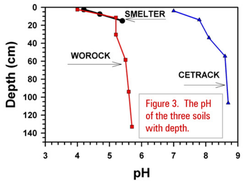


Figure 3. The pH of the three soils with depth.

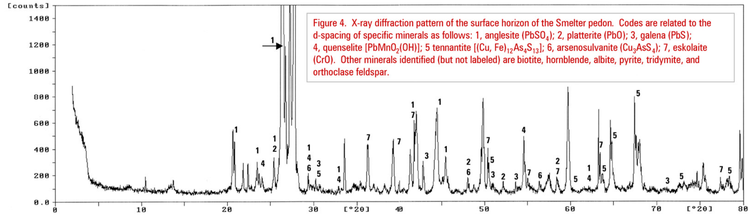


Figure 4. X-ray diffraction pattern of the surface horizon of the Smelter pedon. Codes are related to the d-spacing of specific minerals as follows: 1, anglesite ($PbSO_4$); 2, plattnerite (PbO); 3, galena (PbS); 4, quensenlite [$PbMnO_2(OH)$]; 5 tennantite [$(Cu, Fe)_{12}As_4S_{13}$]; 6, arsenosulvanite (Cu_3AsS_4); 7, eskolaite (Cr_2O). Other minerals identified (but not labeled) are biotite, hornblende, albite, pyrite, tridymite, and orthoclase feldspar.

RESULTS & DISCUSSION

Sequential fractionation (Table 4 a-c) indicates that Cu, Zn, and Pb are partitioned in all fractions of the Smelter pedon and surface horizons (upper 20 cm) of the Worock and Cetrack pedons. Elemental distribution is generally confined to the organic and residual-bound fractions in subsoil horizons of the Worock and Cetrack pedons. These data support the conclusions of Ma and Uren (1998) suggesting that elemental contaminants added to soils initially reside in the more reactive forms (e.g., hydrosoluble, exchangeable) and transform to less reactive forms over time.

The major portion of Cu in surface horizons (Table 4a) was extracted by hydroxylamine hydrochloride (NH_2OH·HCl), suggesting that much of the Cu resides in the oxide fraction, and to a lessor extent in the organic-bound, residual, and exchangeable fractions. Zinc (Table 4b) is generally equally distributed in the organic and residual pools in these upper horizons, with a smaller portion in exchangeable and oxide pools.

The greater proportion of Zn residing in the exchangeable pool in the Worock surface horizon relative to the Cetrack pedon is likely due to the increased solubility of zinc at acid pHs (Romkens and Salomons, 1998; Ma and Uren, 1998).

Lead (Table 4c) is predominately found in the oxide fraction of the Smelter pedon and surface horizons of Worock and Cetrack pedons. In subsoil horizons, Pb is concentrated in the residual fraction. Chromium (Table 4d) is predominately found in the residual fraction. This partition of Cr, along with the lack of elevated amount in surface horizons, suggests that this element is a possible non-contaminant.

Percent recovery (Table 4 a-d) compares the sum of an element solubilized in the sequential extraction process compared to the amount determined by the single total analysis. Most recoveries range from 90 to 125 percent, indicating fairly good agreement between the two methods.

X-ray analysis of the high density, 0.05 to 0.5 mm fraction (Fig. 4) indicates an array of mineral species. Common minerals identified in surface horizons of the pedons were biotite, hornblende, albite, pyrite, tridymite, and orthoclase feldspar.

Crystalline minerals associated with trace elements were anglesite ($PbSO_4$), plattnerite (PbO), galena (PbS), quensenlite [$PbMnO_2(OH)$], tennantite [$(Cu, Fe)_{12}As_4S_{13}$], arsenosulvanite (Cu_3AsS_4), and eskolaite (Cr_2O). These were identified in the surface horizon of the Smelter pedon, but not positively identified in the other two pedons. Limitations of mineral identification by x-ray diffraction include detectable concentrations, crystallinity, and encapsulation by secondary mineral forms.

No evidence of other minerals primarily associated with Cu or Zn [e.g., chalcopyrite ($CuFeS_2$), tennite (CuO), zincite (ZnO)] were found. Limitation of identifying Cu and Zn minerals is likely due to (a) presence of non-crystalline mineral forms, and/or (b) instability of these minerals in soils compared to solution or exchangeable Cu^{+2} or Zn^{+2}, especially at low soil pH (Lindsey, 1979). The surface pH at the Smelter site, which had the greatest trace element concentrations, is 4.1. Lead minerals are generally more insoluble at low soil pH compared to Cu and Zn and have also been identified by Davis, et al. (1992, 1994) in soils of the Butte Mining District.

CONCLUSION

Total analysis indicate the relative concentration of trace elements as Cu > Mn > Zn > Pb > Cd > Cr > Co.

Cu, Cd, Zn, and Pb are elevated in the surface 20 cm of each pedon suggesting these contaminants have only slight mobility in the soil.

Sequential fractionation indicates trace elements added to soils are transformed into a variety of phases, unlike native metals that exist in more resistant (insoluble) forms.

Cu, Zn, and Pb were distributed between various fractions in surface horizons. Proportion of the elements in more easily soluble (e.g., exchangeable) form increased at low soil pH.

Crystalline minerals with trace element composition identified in the heavy density fraction of the Smelter soil were generally associated with Pb. Both primary and secondary minerals were present. These minerals were not as readily identified at the other two sites.

A greater proportion of a trace element in a residual or crystalline form suggests a decreased potential of bioavailability or redistribution as solutes.

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